On the Mechanism of Oxime Formation and Hydrolysis and the Use of the Hydrogen Electrode in the Presence of Certain Organic Compounds.

DISSERTATION.

Submitted to the Board of University Studies of the Johns Hopkins University in conformity with the Requirements for the Degree of Doctor of Philosophy.

By

LUCIUS JUNIUS DESHA

BALTIMORE

1909

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ACKNOWLEDGMENT.

The author wishes to express to President Remsen and to Professors Morse, Jones and Hulburt his appreciation of their instruction in the lecture room and laboratory.

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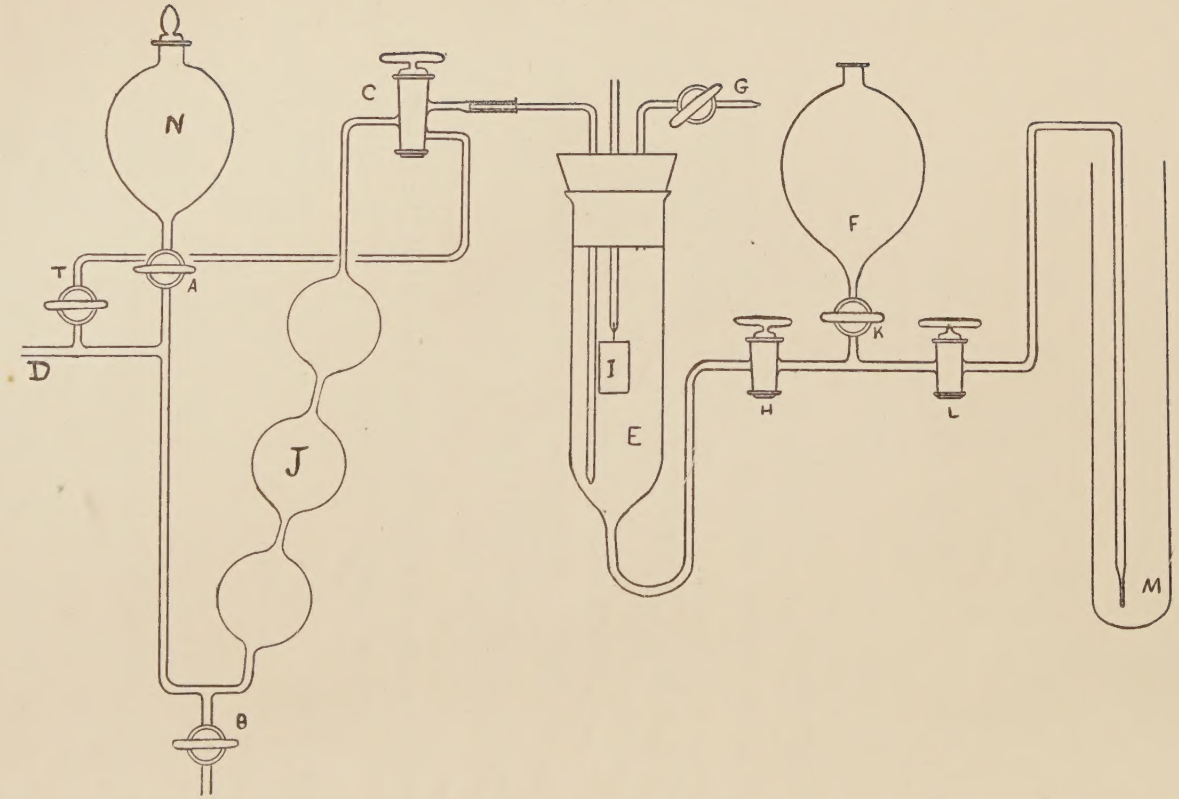

Fig. I

PART 1. ON THE MECHANISM OF OXIME FORMATION AND HYDROLYSIS.

Previous recent papers [1] bearing upon this subject have left several questions still undecided. Barrett and Lapworth [2] have observed the peculiar variation in the velocity of the reaction between one molecule each of hydroxylamine and acetone under the influence of quantities of acid less than one molecule, but have failed to offer an explanation. That the cathion of the oxime formed in this reaction is the real substance existing in equilibrium with the acetone and hydroxylammonium ion, $NH_3\overset{+}{O}H$, is indicated by the work of Acree and Johnson [3] but further evidence is much to be desired. Finally, the catalytic effect of alkali upon the rate of oxime formation, though long known [4], has only been quantitatively investigated in a preliminary way by Barrett and Lapworth [5] and by Acree and Desha. [6]

The present investigation was undertaken in the hope of throwing further light upon these questions and the theories of catalysis which are involved. Having already commenced the work before the appearance of the article by Barrett and Lapworth, I communicated with Professor Lapworth. He agreed "to abandon the further study of the velocity of formation and hydrolysis of oximes, at least for the present, in favour of the American authors," for which consideration I wish to express my appreciation.

The problems suggested will now be considered in the order mentioned.

1. *The cause of the variations in velocity produced by less than one molecule of acid.*

From the data of Barrett and Lapworth, already referred to, it is apparent that the velocity of formation of acetoxime from one molecule each of hydroxylamine and acetone increases rapidly with the addition of acid up to one half molecule. The velocity is a maximum at about this concentration of acid and then decreases at about the same rate with further addition of acid to the point where one molecule of the latter has been added. While the reaction is too rapid in this region for us to be able to obtain velocity constants or any other very exact measurements, the general trend is very apparent from the data cited and from measurements which I have carried out. As the latter only confirm the results of Barrett and Lapworth they need not be given in detail.

1 Lapworth, J. Chem. Soc., 91, 1133. Acree and Johnson: Amer. Chem. J., 38, 258. Acree: Ibid., 39, 300. Barrett and Lapworth: J. Chem. Soc., 93, 85.
2 Loc. cit.
3 Loc. cit.
4 Auwers: Ber. d. chem. Ges., 22, 605.
5 Loc. cit.
6 Acree, Amer. Chem. J., 39, 300.

No simple catalytic action of the acid will account for the sudden rise and subsequent fall in the velocity of oxime formation. An explanation of this can only be found in a consideration of the fact that the total amount of oxime formed is not the result of one reaction, but of several. Considering the conditions prevalent as the initial concentrations of acid are varied from zero to one molecule it is necessary to consider the effect of the change upon the velocity of each of these reactions.

First, there is the reaction between free hydroxylamine and acetone, the course of which may be represented by the expression:

$$\frac{dx_1}{dt} = K_1(C_{acetone})(C_{NH_2OH}) \qquad (1).$$

This reaction is capable of measurement and has been approximately measured in 0.05 N solution at 0.°. Under these conditions it requires something like eight hours to reach completion. Since addition of acid decreases C_{NH_2OH} it is obvious that the velocity of (1) must become even smaller as the concentration of acid is increased, becoming practically zero when one molecule has been added.

Secondly, upon the addition of acid some hydroxylammoniumions, $\overset{+}{NH_3OH}$, will be formed and we may have a second reaction between these and the acetone. This reaction will be more fully discussed later on, but for the present may be expressed:

$$\frac{dx_2}{dt} = K_2(C_{acetone})(C_{\overset{+}{NH_3OH}}) - K'_2(C_{oxime})(C_{HCl}) \qquad (2).$$

The net amount of oxime formation by (2) cannot be directly determined in the region under consideration; that is, when less than one molecule of acid is initially present. When, however, the concentration of acid exceeds one molecule (2) is practically the only reaction taking place. It therefore can be, and has been, measured. The results of these measurements (see Tables XI to XX) with initial concentration of acid varying from one to two molecules indicate that the net amount of hydroxylamine transformed in a given time decreases as the concentration of the acid is increased. This effect is most probably due to the increased velocity of the reverse reaction in (2) which will be obviously accelerated by addition of hydrochloric acid. The maximum transformation due to (2) in the rigion HCl = O and HCl = 1 molecule would lie at the point where the ratio $K_2 : K'_2$ is greatest. Since, however, hydroxylamine is a much stronger base than acetoxime the concentration of the $\overset{+}{NH_3OH}$ ions, and therefore the velocity of the direct reaction would be increased by the first portions of hydrochloric acid much more than the concentration of the oxime cathion, or the (C_{oxime}) (C_{HCl}) which conditions the velocity of the reverse reaction. Judged from this fact alone the maximum net transformation from (2) would occur where considerably more than one-half molecule

of acid has been added. Reaction (2) would not therefore account for the occurrence of the maximum velocity when just about one-half of a molecule of acid is added, nor is there any reason to suppose from the other data that it would produce as great a velocity as is found at this concentration. It should be borne in mind, however, that if the velocity of the reverse reaction were intrinsicly greater than that of the direct one, the maximum of net transformation *might* lie at the point where it is found. A determination of the velocity constants for the two opposing reactions would be necessary to settle this point.

Finally, there is a third reaction which has been supposed by Lapworth and Barrett and by Acree to proceed under these conditions, namely, that in which the free hydroxylamine unites with the small amount of the cathion of acetone which is formed upon the addition of acid. That carbonyl compounds in general unite to a certain extent with acids in solution to form salts and consequently cathions has been shown very conclusively by a large amount of work on the subject [1]. Such action of the acetone in this case would make possible a reaction which may be expressed

$$\frac{dx_3}{dx} = K_3 \, (C_{NH_2OH}) \, (C_{(CH_3)_2CO.\overset{+}{H}}) \qquad (3).$$

From the fact that acetone is an extremely weak base, as compared with hydroxylamine, it is apparent that only a very small amount of the cathion of the former could exist in solution when the two bases are in competition for a given amount of acid. Nevertheless if (3) is a very rapid reaction, even this small amount of acetone cathion could account for the maximum velocity observed in the measurement of total oxime formation. A consideration of the conditions which would cause the most rapid formation of oxime by (3) will make this clearer.

The amount of transformation by (3) is proportional to the product of (C_{NH_2OH}) and $(C_{(CH_3)_2CO.\overset{+}{H}})$ and we may calculate the conditions under which this product will have its maximum value. If we have one molecule each of free hydroxylamine and of acetone in solution and add 0.1 molecule of acid the latter divides itself between the two bases. If y represents the small amount of acetone cathion formed, $0.1-y$ will represent approximately the amount of $NH_3\overset{+}{O}H$ formed and the concentration of free NH_2OH is reduced from the original value of 1 to $1-(0.1-y) = .9 + y$. Then (C_{NH_2OH}) $(C_{(CH_3)_2CO.\overset{+}{H}}) = (.9 + y)\,(y) = .9\,y + y^2$ With further addition of acid this product will change as shown in the following:

1 For a full list of references upon this work see Acree and Johnson: Amer. Chem. J. 38, 298. Their own work showing that the addition of carbonyl compounds lowers the conductivity of hydrochloric acid solutions is also significant in this connection.

TABLE I.

mols HCl added	$C_{(CH_3)_2CO.\overset{+}{H}}$	C_{NH_2OH}	*Product*
0.0	0	1.	$0 \quad (1)=0.$
0.1	y	.9+ y	$y\ (.9+1y)=0.9y+\ y^2$
0.2	2y	.8+2y	$2y\ (\ 8+2y)=1.6y+\ 4y^2$
0.3	3y	.7+3y	$3y\ (.7+3y)=2.1y+\ 9y^2$
0 4	4y	.6+4y	$4y\ (.6+4y)=2\ 4y+15y^2$
0.5	5y	.5+5y	$5y\ (.5+5y)=2.5y+25y^2$
0.6	6y	.4+6y	$6y\ (\ 4+6y)=2.4y+36y^2$

Disregarding y^2 in the above products as negligibly small, it becomes apparent that the product of the concentrations of free hydroxylamine, and of acetone cathions must be a maximum when one-half molecule of acid is added, and therefore the velocity of transformation will be greatest under this condition. This prediction is in harmony with the experimental fact brought out by Barrett and Lapworth[1] that the total rate of oxime formation is greatest when about one-half molecule of acid has been added. Such agreement of the fact is certainly a strong argument in favour of the theory which calls for it.

Finally, it must be remembered that the total rate of change experimentally measured is the sum of the transformations by (1), (2) and (3). Therefore, though (3) probably predominates, the influence of (1) and (2) will be such that the curve representing the total rate of transformation will not have the exact slope and maximum which would be calculated from Table I, if reaction (3) were alone concerned.

2. *On the real equilibrium in acid solution.*

When hydroxylamine hydrochloride reacts with a ketone in solution, either alone or in the presence of an excess of hydrochloric acid the predominating reaction is most probably that between the ketone and the hydroxylammoniumion, $NH_3\overset{+}{O}H$, which has been expressed in (2). This view is supported by the fact that hydroxylamine hydrocloride is only slightly hydrolyzed [2] (0.74 per cent. in N/32 solution), and that this small amount is largely suppressed by the addition of any free acid. The concentration of free hydroxylamine in such a solution would accordingly be so small as to render improbable any considerable transformation by the reaction between this substance and the cathion of the ketone present.

The reaction, which is reversible, may then be considered to take place in the following manner:

[1] Loc. cit.
[2] Winkelblech: Z. physik. Chem. 36, 574.

$$R_2CO + NH_3OH^{+} + Cl^{-} \leftrightarrows R_2C.OH.NH_2OH^{+} + Cl^{-} \leftrightarrows$$
$$R_2C{:}NOH\ H^{+} + Cl^{-} + H_2O \leftrightarrows R_2C{:}NOH + H^{+} + Cl^{-} + H_2O \qquad (4).$$

If we start with one molecule each of hydroxylamine hydrochloride and ketone, the direct reaction may then be expressed:

$$\frac{dx}{dt} = K_{trans}\,(C_{R_2CO})\,(C_{NH_2OH.HCl})\,\alpha \qquad (5)$$

where α is the percentage dissociation of the hydroxylamine hydrochloride. Disregarding the water formed in the reaction, the active mass of the water present at these dilutions being practically constant, the end products of the reaction are HCl and $R_2C{:}NOH$. The reverse reaction would then be expressed by

$$-\frac{dx}{dt} = K'_{trans}\,(C_{R_2CO:NOH})\,(C_{HCl})\,\alpha' \qquad (6)$$

where α' is the percentage dissociation of the hydrochloric acid. If A is the initial concentration of ketone and hydroxylamine, $A-x$, the amount present at time t, and (5) and (6) are combined with these value substituted, we have

$$\frac{dx}{dt} = K_{trans}\,(A-x)^2\,\alpha - K'_{trans}\,x^2\,\alpha' \qquad (7);$$

when equilibrium is established

$$\frac{\alpha(A-x)^2}{\alpha' x^2} = \frac{K'_{trans}}{K_{trans}} = K_{equil} \qquad (8).$$

If an amount of free hydrochloric acid equal to B be initially added to the reaction mixture, the active mass of acid influencing the reverse reaction becomes $\alpha'(x+B)$ instead of $\alpha' x$ and (8) becomes

$$\frac{\alpha(A-x)^2}{\alpha' x(x+B)} = K_{equil} \qquad (9).$$

The amount of hydroxylamine hydrochloride, x, which has disappeared as a result of the reaction may be determined at any time by the analytical method. If, as we have so far assumed, the intermediate reaction products represented in equation (4) exist only in inappreciable quantities the amount of free oxime and of hydrochloric acid formed as a result of the reaction will each be equal to this same x. B, the amount of free acid added, is known in each case. Therefore we may obtain the data for calculating the value of K_{equil} from (9). According to the mass law this value must remain constant irrespective of the amount of free acid added if the assumptions used in formulating (9) are correct.

That the value of K_{equil} does not remain constant with addition of acid is clearly indicated by Tables III to VIII, in which the results of measurements of the equilibrium under various conditions are recorded. The point of equilibrium is observed to vary markedly with the temperature, with the individual ketone used and with the concen-

tration of the catalyzer. The last is of especial significance as emphasizing the fact already pointed out[1] that under certain conditions the third law of catalysis (that a change in the concentration of the catalyzer does not change the equilibrium point in reversible reactions) does not hold good. But the important fact brought out by Tables III to VIII is the very pronounced falling off in the values of the equilibrium constant which is manifested. In every series this decrease is pronounced, amounting to from 27 to 45 per cent. between the concentrations of acid studied—one and two molecules.

The values of α' (the percentage dissociation of HCl) are calculated from the Kohlrauch-Holbern Tables. To obtain α for $NH_2OH.HCl$ the values found by Bredig[2] and Winkelblech[3] were plotted and the curves extraprolated, where necessary, by assuming that they would follow the same general course as that for a salt like potassium chloride. The mean of the values thus obtained from the results of these two workers was taken and may be regarded as correct, certainly to within one per cent. But even if the errors were greater, the general nature of the results would not be affected. No values were obtainable for the dissociation of $NH_2OH.HCl$ at 0°, so the same values of α and α' were used in the calculations for that temperature as for 25°. The relative percentage of dissociation of the two chlorides would vary so slightly between these temperatures that no sensible error is introduced.

The suppression of ionization of the hydrogen chloride and the hydroxylamine chloride by one another was calculated upon the Barmwatter[4] hypothesis that if a molecules of one salt and b of another furnishing a common ion are in solution together, the former will be dissociated to the extent it would be if dissolved alone in $\frac{a}{a+b}$ of the given volume. The percentage ionization will of course remain unchanged during a given reaction. The following values have thus been derived and used in the calculation for Tables III to VIII.

TABLE II.

1 mol. NH_2OH + n mols. HCl in 40 litres.

Mols. HCl	α' (for HCl)	α (for $NH_2OH.HCl$)
1.00	97.00%	88.8%
1.25	96.7 %	88.2%
1.50	96.3 %	86.7%
2.00	95.0 %	83.8%

[1] Acree and Johnson: Amer. Chem. J., 38, 351.
[2] Z. physik. Chem., 13, 223.
[3] Ibid, 36, 574.
[4] Z. physik. Chem., 28, 424; 45, 557; 56, 225.

TABLES III TO VIII.

		mols. HCl	A-x	x	B	$\frac{a(A-x)^2}{a^1 x(x+B)}$	Δ	Unchanged NH_2OH
III.	1 mol. acetone, 1 mol NH_2OH, *n* mols. HCl in 20 litres. A, 0.05. Temperature, 0°.	1.00	.01507	.03493	0	.186*		30.15%
		1.25	.01677	.03323	.0125	.185*		33.55%
		1.50	.0177	.03230	.0250	.169*		35.39%
		2.00	.01861	.03139	.0500	.135*	27.42%	37.23%
IV.	1 mol. acetone, 1 mol. NH_2OH, *n* mols. HCl in 40 litres. A, 0.025. Temperature, 25°.	1.00	.01116	.01384	0	.596		44.65%
		1.25	.01210	.01290	.00625	.528		48.40%
		1.50	.01273	.01227	.01250	.481		50.92%
		2.00	.01313	.01187	.02500	.419.	29.70%	52.53%
V.	1 mol. methyl ethyl ketone, 1 mol. NH_2OH, *n* mols. HCl in 40 litres. A, 0.025. Temperature, 0°.	1.00	.01135	.01365	0	.634		45.41%
		1.25	.01224	.01276	.00625	.563		48.95%
		1.50	.01287	.01213	.01250	.500		51.50%
		2.00	.01378	.01122	.02500	.412	34.94%	55.13%
VI.	1 mol. methyl ethyl ketone, 1 mol. NH_2OH, *n* mols. HCl in 40 litres. A, 0.025. Temperature, 25°.	1.00	.01368	.01132	0	1.339		54.73%
		1.25	.01457	.01043	.00625	1.113		58.28%
		1.50	.01543	.00957	.01250	1.015		61.73%
		2.00	.01644	.00856	.02500	0.830	38.01%	65.77%
VII.	1 mol. diethyl ketone, 1 mol. NH_2OH, *n* mols. HCl in 40 litres. A, 0.025. Temperature, 0°.	1.00	.01573	.00927	0	2.636		62.90%
		2.00	.01854	.00646	.025	1.491	43.44%	74.16%
VIII.	1 mol. diethyl ketone, 1 mol. NH_2OH, *n* mols. HCl in 40 litres. A, 0.025. Temperature, 25°.	1.00	.01698	.00802	0	4.104		67.90%
		2.00	.02004	.00496	.025	2.264	44.83%	80.15%

*Values for a and a^1 not introduced in calculating these constants on account of uncertainty of data for this concentration of acid.

In these tables under *mols. HCl* is given the number of molecules of acid initially present for one of ketone or hydroxylamine; under B is the molecular normal concentration of the acid *free* at the beginning of the reaction. $A-x$ has the usual significance. The figures under $\frac{a(A-)x^2}{a'x(x+B)}$ are the values of the equilibrium constant obtained by inserting the proper values in that expression. Δ indicates the percentage decrease in the value of the equilibrium constant when two molecules of acid are added, from its value with only one. The last column represents the percentage of the original amount of NH_2OH remaining when equilibrium has been established.

This explanation of these changes in the equilibrium constants shown by Tables III to VIII can only be explained by the fact that we are not dealing with the real equilibrium. Heretofore, it has been assumed that the salt or cathion of the oxime formed is practically completely hydrolyzed and therefore that the real equilibrium is that between the ketone and hydroxylamine cathion upon the one side and these hydrolysis products, free oxime and hydrochloric acid, on the other. The constants were calculated on that basis, and the fact that they decrease with addition of free hydrochloric acid indicates that this assumption is not correct, and that the active mass of the acid is not directly concerned in the equilibrium. In other words, in order that the mass law may hold, the cathion of the oxime must be present in a measurable amount and the latter is the substance really in equilibrium with the ketone and hydroxylammonium ion.

If now in time t, x is the net amount of ketone and hydroxylamine which have disappeared in the reaction, the total amount of oxime salt formed will also be x. Let y equal the portion of this which is not hydrolyzed. Then if a'' is the percentage of ionization of the oxime hydrochloride $a''y$ equals the concentration of the oxime cathion at any time. But this is the only substance undergoing change in the reverse reaction and therefore this is to be represented by

$$\frac{dx}{dt} = K''_{trans}\, a''\, y \qquad (10).$$

(7) then becomes

$$\frac{dx}{dt} = K_{trans}\,(A-x)^2\, a - K''_{trans}\, a''y \qquad (11)$$

and (8) becomes

$$\frac{(A-x)^2\, a}{a''\, y} = K_{equil} \qquad (12)$$

Unfortunately K_{equil} cannot be directly calculated from (12) since no very satisfactory means[1] of measuring y is available. I have,

[1] Attempts to apply cane sugar inversion experiments and the potential of the hydrogen electrode for this purpose are described later on in this article.

however, been able to approximate it by the following means: If x is the total oxime formed and y of this remains unhydrolyzed, $(x—y)$ is the amount of free oxime and free acid formed in the reaction. If B is the amount of free acid added as catalyzer, the concentration of hydrogen ions will be $a'(x-y+B)$ Substituting these values in the usual expression for the hydrolysis of a cathion

$$K_{hyd} = \frac{(C_{acid})\ (C_{base})}{C_{cathion}}$$

we have

$$K_{hyd} = \frac{a'(x-y+B)\ (x-y)}{a''y} \qquad \text{or, } a''y = \frac{a'\ (x-y+B)\ \ (x-y)}{K_{hyd}} \tag{13}$$

Substituting this value for y in (12) we obtain

$$\frac{(A-x)^2}{(x-y+B)\ (x-y)} = \frac{K_{equil}}{K_{hyd}} = K \tag{14}$$

From the data obtained, Table V, with .025 N methyl ethyl ketone and hydroxylamine hydrochloride reacting at 0° under the influence of different amounts of acid, I have calculated what value y must have in each case in order that K_{equil} as calculated from (12) may remain constant. These values must further fulfill the condition that when substituted in (13) they will give a real constant for the value of K_{hyd} at all concentrations of acid. By a series of approximations it was found that if $K_{equil} = .022$, y must have the following values in order for (12) to hold good.

TABLE IX.

mols HCl (initial conc.)	A—x (found by experiment)	y (calculated)
1.0	.01135	.005859
1.25	.01224	.006761
1.50	.01287	.007357
2.00	.01378	.008145

(Not knowing the value of a'' I have assumed in these calculations that it is equal to a ; certainly they will both vary in nearly the same way, so that this assumption will at most only modify K_{equil} by a constant term.)

Substituting in (13) these calculated values of y with the other data obtained by experiment, the results for the hydrolysis constant of methyl ethyl ketoxime are obtained.

TABLE X.

mols HCl	a'	x	y	$a=a''$	B	K_{hyd}
1.00	.97	.01365	.005859	.888	0	.01134
1.25	.967	.01276	.006761	.882	.00625	.01183
1.50	.963	.01213	.007357	.867	.01250	.01215
2.00	.950	.01122	.008145	.838	.02500	.01134
						.0116

Since the hydrolysis constant calculated in this manner is really so nearly a constant and, as may be readily verified, varies so widely when any other value than .022 is assumed for K_{equil} in (12) we are justified in regarding this as the true value of the constant expressing the true equilibrium between the ketone, hydroxylammonium ions and oxime cathions. From Table X it is apparent that in a solution containing initially one molecule each of methyl ethyl ketone and hydroxlyamine and two of hydrochloric acid the non-hydrolyzed portion of the oxime equals $\frac{y}{x} = \frac{.008145}{.01122} = 72.6$ per cent. of the total oxime formed; hence the concentration of the oxime cathion in such a solution is $a'' .726x = .608\,x$. That is, the oxime cathion exists to about 60.8 per cent. of the total oxime formed.

Inserting the average value of $K_{hyd} = .0116$ (Table X) and K_{equil} .022 in (14) we obtain $K = 1.9$ as the equilibrium constant between the end products.

Measurements of the velocity of transformation were made in a number of cases. When this data is substituted in the integral of (7) the values of K_{trans} obtained show a decided drift all the way through, still further substantiating that (7) does not express the real nature of the reaction. If (11) can be integrated and the proper data substituted real velocity constants should be obtainable for both the direct and reverse reactions. I have not as yet been able to obtain an integral of (11) so that I am unable to make these calculations. However, I will record a few of the measurements which may be inserted in the proper integral when found. The results are embraced in Tables X to XX, which will be given after a description of the analytical method employed in obtaining them and also Tables III to VIII.

Analytical Method.

A single large lot of Kahlbaum c. p. hydroxylamine hydrochloride was used. On analysis it proved to be sufficiently pure.

.3220 gm. gave .6624 gm. AgCl = 50.89% Cl = 99.74% $NH_2OH.HCl$.

.3377 gm. gave .6949 gm. AgCl = 50.90% Cl = 99.77% $NH_2OH.HCl$. ($NH_2OH.HCl$ = 51.02% Cl).

To prepare the solutions 1.9113 gms. of this salt were dissolved in 500 cc. of conductivity water, giving a .055 normal solution.

The ketones were obtained from Kahlbaum and redistilled after drying over calcium chloride. To prepare the solutions a 250 c.c. graduated glass stoppered flask was half filled with conductivity water and weighed on a balance sensitive to 0.2 milligram. A slight excess over the amount of ketone necessary to prepare a .055 N solution was measured in by the aid of a one cc. pipette graduated to hundredths, the flask reweighed, filled to the mark at the proper temperature and the amount of water necessary to give an exactly .055 N solution measured in from a burette.

The standard normal hydrochloric acid used was prepared by absorbing hydrochloric acid gas (from fused ammonium chloride and concentrated sulphuric acid) in conductivity water, and further standardized by precipitating and weighing the silver chloride.

Reaction mixtures were prepared as follows: For the cases where no extra acid was to be added, 20 cc. of water, 100 cc. of .055 N $NH_2OH.HCl$ and 100 cc. of .055 N ketone solutions were quickly mixed in a dry flask, giving 220 cc. of a solution initially .025 N with respect to the reacting substances. The individual solutions had been brought to the proper temperature before mixing and afterwards the mixtures were maintained at constant temperatures by the use of an ice bath for 0° and an electrically regulated bath for 25°, constant to within 0.01. When acid was to be added the amount of a normal solution of HCl necessary to give 220 cc. of solution containing ¼, ½ or 1 molecule of .025 N acid was added to the flask. The 20 cc. of water added in the other case was of course suitably diminished so that the total volume should still be 220 cc.

Twenty cubic centimeter portions were withdrawn at definite intervals and poured into an excess of iodine solution in disodium hydrogen phosphate and the excess of iodine titrated with thiosulphate. As previous workers have found, the titration is not as accurate as could be desired. Magnesia, sodium acetate and disodium hydrogen phosphate of various concentrations were all tried and finally 10 cc. of a solution of the latter, saturated at room temperature, was found to give the least unsatisfactory results under all conditions.

Owing to the rapid changes in the strength of iodine and thiosulphate solutions no attempt was made to keep a record of their absolute values. They were made approximately twentieth normal (two atoms of iodine are required for one molecule of NH_2OH by the reaction

$$2\,NH_2OH + 2\,I_2 = N_2O + H_2O + 4\,HI\,)$$

and these compared with .025 N solution of the hydroxylamine hydrochloride made up exactly as described for the measurement of velocities, but containing, of course, only the hydroxylamine and pure water. The following are fair samples of the values so obtained:

20 cc. .025 N $NH_2OH.HCl$ required of iodine solution:

22.07	22.33	21.74
22.07	22.28	21.76
21.99	22.25	21.71
22.02	22.32	21.80
21.96	22.26	.....
Average, 22.02	22.29	21.75

Such a check was made at least once a week; all titrations in the meanwhile being oriented from the last average value so found.

The amount of hydroxylamine remaining at equilibrium was determined by preparing solutions just as for measuring velocities, allowing the reaction to proceed to equilibrium at the temperature in question and then titrating five or six twenty cc. portions and taking the mean value. The equilibrium constants may then safely be regarded as correct to within 0.3 to 0.5 per cent. in the cases of methyl ethyl and diethyl ketones. As regards acetone, I feel less sure on account of its great vapour tension, though every effort was made to have the flasks open as little as possible.

The measurements of the amount of hydroxylamine present at any time *during* a reaction is much less satisfactory. Obviously, duplicate values cannot be obtained with such a rapid reaction; moreover, the titration is apparently affected by the relative amounts of the iodine and hydroxylamine present and the volume of the solution, and these cannot be maintained constant as in determining the initial and equilibrium values. However, by running duplicates and plotting the titration results against the time the more accurate values form a fairly regular curve, and those falling far from it may be disregarded as vitiated by errors in titration, reading of the time, etc. No such values have been discarded in the tables, however, unless known to be incorrect for some reason. All of the velocity measurements were carried out at zero since the reactions are too rapid to follow at 25°.

TABLES XI TO XX.

Tables XI to XIV were measured with solutions containing initially one molecule each of $(CH_3)_2CO$ and $NH_2OH.HCl$ plus 0, ¼, ½ and 1 molecule respectively of free HCl in 20 litres. *A*, therefore, equals .05 in each case. *B* equals normality of free HCl initially present.

XI B, 0		XII B, 0.0125		XIII B, 0.025		XIV B, 0.05	
t	A−x	t	A−x	t	A−x	t	A−x
4.3	.0336	3.2	0.4058	3.1	.04527	4.	.04605
11.5	.02684	7.5	.03571	7.3	.04012	8.2	.04324
18.3	.02422	12.7	.03152	20.1	.03369	19.4	.03925
23.9	.02247	35.8	.02367	75.7	.02247	36.9	.03313
30.	.02082	46.8	.02142	97.3	.02015	60.9	.02817
40.7	.01866	92.7	.01804	110.3	.01923	83.9	.02505
55.3	.01806	126.7	.01689	150.3	.01788	116.9	.02256
73.6	.01634	(*equil*)	.01677	(*equil*)	.01769	(*equil*)	.01861
90.	.01556						
(*equil*)	.01507						

Tables XV to XVIII are for 1 mol. $C_2H_5CO\,CH_3$ plus 1 mol. $NH_2OH.HCl$, plus 0, ¼, ½ and 1 mol. respectively, of HCl in 40 litres. Temp., 0°; A, .025

XV		XVI		XVII		XVIII	
a', 0.97		a', 0.967		a', 0 963		a', 0.95	
B, 0		B, 0.00625		B, 0 0125		B, 0.025	
a, 0.888		a, 0.882		a, 0.867		a, 0.838	
t	A−x	t	A−x	t	A−x	t	A−x
2.5	.01985	3	.02154	3.2	.02323	1.9	.02363
6.	.01746	8.6	.01890	6.8	.02145	4.	.02298
11.2	.01550	12.9	.01746	11.3	.01987	7.4	.02211
15.9	.01446	16.6	.01656	15.0	.01914	10.	.02121
20.2	.01382	20.7	.01576	20.8	.01762	15.9	.02013
26.1	.01312	26.2	.01513	26.9	.01677	19.5	.01953
31.7	.01273	33.9	.01441	33.1	.01618	23.5	.01893
41.9	.01232	39.7	.01392	40.9	.01540	30.6	.01795
61.7	.01185	58.2	.01298	46.7	.01509	42.	.01680
80.5	.01152	90.	.01258	61.8	.01409	93.	.01458
(*equil*)	.01185	(*equil*)	.01224	(*equil*)	.01287	(*equil*)	.01378

Tables XIX and XX are for 1 mol. $(C_2H_5)_2CO$ plus 1 mol. $NH_2OH.HCl$, plus 0 and 1 mol., respectively, of HCl in 40 litres. Temp., 0°; A, .025 .

XIX			XX		
a', 0.97	B, 0	a, 0.888	a', 0.95	B, 0.025	a, 0.838
t		A−x	t		A−x
2.2		.02190	1.7		.02454
4.3		.02050	4.6		.02389
8.6		.01877	8.8		.02316
12.		.01808	12.1		.02263
15.7		.01736	17.3		.02226
20.5		.01679	26.9		.02087
24.3		.01634	33.1		.02047
27.6		.01628	49.		.01971
32.7		.01586	78.5		.01900
36.5		.01590	106.1		.01864
(*equil*)		.01576	(*equil*)		.01854

Indirect Measurement of Oxime Salt Concentration by the Inversion of Cane Sugar.

Having shown that the oxime cathion is the real substance existing in equilibrium with the hydroxylamine salt and the ketone, and calculated its probable concentration, I endeavored to get confirmatory evidence by other measurements. Direct determination of this ion being impracticable the most hopeful method appeared to be the determination of the free hydrogen ion concentration by one of the known methods, and from this, by difference, the amount of acid used up in the formation of this cathion. An extensive series of measurements, made in an endeavour to use the potential of the hydrogen electrode (Part II of this article) for this purpose, gave no significant results. The same object was then sought by measuring the velocity of the inversion of cane sugar by the reaction mixtures.

For the experiments a quantity of a 20 per cent. solution of cane sugar, to which had been added 0.005 per cent. of thymol, was prepared and used throughout the series. Ten cc. of this solution was in each case added to an equal volume of the dilute acid or acid plus other substance, as the case might require. The change of volume on mixing was not considered, for besides being small in itself it would be practically the same for 10 cc. of sugar solution plus 10 cc. of pure water as for 10 cc. of sugar solution plus 10 cc. of any of the solutions added, since the latter were never more than 0.1 N in salt content even adding all the foreign substances present. While not in the polarimeter the tubes were maintaind in closed vessels in a 25° constant temperature bath. With such dilute solutions the few degrees change in temperature during the time necessary to make a reading is negligible. It would have been preferable to make these measurements at 0°, since the velocity of oxime formation was determined at that temperature, but the moisture which immediately collected on the glass ends of the polarimeter tube when removed from a zero bath made reading impossible. It might have been obviated by a rather complex arrangement for providing the ends with caps containing dry air, but lack of time prevented further experiment along this line. The inversion velocity at that temperature would have been inconveniently slow; even at 25° it was necessary in general to calculate the final reading by the usual formula rather than wait from two to six weeks for it to be obtained.

The velocity of inversion by different concentrations of pure hydrochloric acid was first measured under these conditions and gave the following results.

TABLE XXI.

No.	conc. of HCl	K
1	0.0125	.000036
2	0.025	.000078
4	0.05 N	.000171

The results[1] agree with the observations of Arrhenius[2] and others that at these concentrations the acceleration is not exactly proportioned to the active mass of the acid. The values obtained were plotted and the inversion velocity which would be produced by other concentrations of acid determined by interpolation. Mixtures of hydrochloric acid with hydroxylamine and methyl-ethyl ketone were then employed. Under "concentration" is given the normality of the solution actually used in the polarimeter tube, with respect to each constituent.

TABLE XXII.

No.	Concentration			K
	HCl	$NH_2OH.HCl$	Ketone	
7	0.025	0.0125	0	.000086
9	0.025	0	0.0125	.000084
10	0.025	0	0.00975	.000082
11	0.025	0.025	0.025	.000103
12	0.0	0.025	0.025	.000030

These results from 7, 9 and 10, Table XXII, indicate that the ketone and hydroxylamine exercise about the influence which would be expected from neutral substances, not reacting with the sugar. That they do not unite with the sugar or glucose at these dilutions is not proven. It is, however, rendered highly probable from the facts that both exercise about the same influence, that in the cases where the end point was waited for it agreed with that calculated and that velocity constants were about equally good at all stages of the reaction. Two sets of the measurements may be given to show the range of error.

TABLE XXIII.

A 19°.09			A, 19°.18		
t	A−x	K	t	A−x	K
200	18.83	0.0000298	222	18.07	0.000121
1440	17.31	295	605	16.28	118
1680	16.96	304	1255	13.70	117
3101	15.41	300	1728	12.03	117
4638	13.93	295	2848	8.98	120
5597	12.99	299	3121	8.17	119
7126	11.50	309	4128	6.13	120
9912	9.54	304	4680	5.38	118
			5623	4.16	118
	Average,	0.0000300	7028	2.85	118
			9907	1.41	115
			12777	.75	110
				Average,	0.000118

1 All the values of K which I give for sugar inversion are to be divided by the logarithm factor 0.4343.

2 Z. physik. Chem., 4, 244.

Now consider inversion No. 11, Table XXII. We can calculate what the velocity should be in this case from the following considerations: As the result of independent equilibrium measurements[1] it is known that a mixture of one molecule each of hydroxylamine hydrochloride, methyl ethyl ketone and hydrochloric acid is in equilibrium at 25° when 65.77 per cent. of the hydroxylamine hydrochloride remains and 34.23 per cent. of oxime hydrochloride has been formed. Assuming complete hydrolysis of the oxime salt, the concentration of acid at equilibrium would therefore be $(1 + .3423)\ 0.025 = 0.03356$. From the curve obtained from Table XXI this acid would give a velocity constant, K, = .0001095.

This does not, however, take into consideration the effect of the neutral substances present. From inversions 7, 9 and 10 (Table XXII) 12 per cent. is probably a fair enough average figure to take for the effect of these substances to be considered. Each molecule then of hydroxylamine, of ketone and of oxime (free, salt or cathion) present would increase the velocity by 12 per cent. of that due to one molecule of acid; that is, 12 per cent. of 78 units, or 9.4 units. At equilibrium 0.65 molecule each of hydroxylamine and ketone and 0.35 molecule of oxime (in some form) are present. Therefore

Velocity due to $NH_2OH.HCl = (0.65)x(9.4) =$	.000006
Velocity due to ketone $= (.065)x(9.4) =$	.000006
Velocity due to oxime $= (.35)x(9.4) =$	.000004
Velocity due to HCl =	.0001095
Velocity calculated	.0001255
Velocity found (Inversion 11, Table XXII)	.000103
	.0000225

This discrepancy must be caused by the removal of part of the free hydrochloric acid in the formation of oxime cathions, Recalling that

Velocity calculated for .03356 N HCl = .0001095 and
Velocity measured for .025 N HCl = .000078

.0000315

this difference of 0.0000315 is the increment if *all* the oxime were hydrolysed. But the inversion value found, 0.000103, shows an increment due to the acid thus derived of only 0.0000315 less 0.0000225 or 0.000009 units; $\frac{0.0000090}{0.0000315} = 28.5$ per cent. of oxime hydrolyzed; the oxime therefore exists as total salt to to the extent of 71.5 per cent. according to these figures. Considering all things, this is in very good agreement with the value calculated from the equilibrium data (Tables V and X), which indicated 72.6 per cent. of oxime salt present under the same conditions of concentration.

[1] Table VI.

Taken as a whole this result is of decided importance. It certainly substantiates the conclusion to which we are forced by the equilibrium data, namely, that the cathion of the oxime hydrochloride exists in the solutions in much larger quantity than has been suspected, and that it is this intermediate compound which really undergoes transformation when hydroxylamine salt and a ketone are formed from an oxime.

3. *Alkali Catalysis.*

Some experiments looking toward the solution of the mechanism of the reaction when free hydroxylamine and ketones unite in the presence of alkali constituted the first work undertaken in this research. I started with the opinion that the alkali probably forms the well known salts of acetone or hydroxylamine according to the following, or some similar, reaction:

$$(CH_3)_2CO + NH_2OH + KOH \rightleftarrows (CH_3)_2CO + NH_2\overset{-}{O} + \overset{+}{K} + H_2O \rightleftarrows$$

$$(CH_3)_2C.NOH.\overset{-}{O}H + \overset{+}{K} \rightleftarrows (CH_3)_2C{:}\overset{-}{N}O + \overset{+}{K} + H_2O \rightleftarrows$$

$$(CH_3)_2C{:}NOH + \overset{+}{K} + \overset{-}{O}H.$$

Work was planned which should have indicated whether this or some other view were correct, but after having made some twenty measurements of the velocity of the reaction with different concentrations of alkali my attention was diverted by other phases of the problem and I have not as yet been able to investigate this question as thoroughly as I had hoped to do. The results presented are therefore of a preliminary nature, but seem to have some significance.

The method employed was essentially the same as that with acid solutions. Solutions of free hydroxylamine were prepared by the addition of the theoretical volume of standard sodium hydroxide solution to a weighed quantity of pure hydroxylamine hydrochloride; attempts to titrate in the correct amount of alkali by the use of phenolphthalein showed the latter procedure to be unreliable. In one series the portions of the reaction mixture withdrawn were titrated as usual with iodine in the presence of hydrogen disodium phosphate, enough acid being always added to the iodine simultaneously with the reaction mixture to neutralize the alkali present as catalyzer in the latter.

In another series a new method of determining the amount of transformation was employed. Hydroxylamine, a strong base, requires the addition of nearly the theoretical molecular quantity of hydrochloric acid before the solution becomes acid to methyl orange or Congo red. Acetoxime solutions give an acid reaction with the same indicators when only about 1.3 per cent. of the equivalent amount of mineral acid is added. The method employed depends upon this dif-

ference. Portions of the reaction mixture were pipetted out at intervals, poured into a large volume of ice cold distilled water and rapidly titrated with tenth normal hydrochloric acid in the presence of Congo red. The amount of oxime formed was given by the volume of acid required after this had been corrected for the amount used up by the alkali present as catalyzer, and for the very small amount of acid required by a quantity of oxime equal to that thus approximately found present. The method is open to the objection that the reaction is only retarded and not stopped when the volume is largely diluted. More important, however, is the change which goes on during titration. For while acid is being added to convert all the hydroxylamine into its hydrochloride the conditions are favorable to the very rapid formation of oxime by reaction (3) which is discussed in Section 1. To avoid this action as much as possible what was estimated to be nearly the required amount of acid was added at once. Then, quickly, but with more care, as much more acid was added as was required to give the same colour as a standard comparison solution prepared by adding the same amount of Congo red to a solution of pure hydroxylamine hydrochloride.

The results of some of the measurements are recorded in the following tables. Acetone was used in every experiment and all reactions were carried out in an ice bath. Immediately after mixing, each solution was .05 N with respect to acetone and to free hydroxylamine (therefore $A = .05$ in every case) and contained in each 110 cc. of total volume the number of cubic centimeters of 0.1 N sodium hydroxide solution indicated in each case. The values of K are calculated from the usual expression $K = \frac{x}{A\,t\,(A-x)}$ The experiments recorded in Tables XXIV to XXVIII were carried out by the method of acid titration; those in XXIX to XXXI by the iodine method.

XXIV.			XXV.			XXVI.		
1.5 cc NaOH			3 cc NaOH			6 cc NaOH		
t	A−x	K	t	A−x	K	t	A−x	K
2.5	.04718	.478	8.	.0393	.68	4.2	.03505	2.04
12.	.04574	.156	16.9	.0340	.56	14.2	.02515	1.392
27.	.04426	.096	31.7	.0297	.432	21.2	.02565	.896
48.5	.03995	.104	40.5	.02685	.43	27.7	.01915	1.090
61.7	.03703	.114	54.5	.02545	.354	35.7	.01535	1.294
75.5	.03641	.098	61.	.0229	.398	42.2	.01410	1.196
96.	.03359	.102	69.	.0226	.352	52.2	.01220	1.188
115.5	.03046	.112	84.	.0209	.338	65.5	.01090	1.096
128.5	.03031	.102	113.	.0172	.336	86.7	.00825	1.168
			133.5	.0156	.330	107.7	.00715	1.138

XXVII.

9 cc NaOH

t	A–x	K
7.4	.0204	2.62
11.8	.01985	2.58
15.2	.01775	2.40
18.	.0163	2.30
24.	.0144	2.06
30.7	.0121	2.04
40.2	.01015	1.95
50.7	.0095	1.85
66.4	.00615	2.14
119.5	.0036	2.16

XXVIII.

12 cc NaOH

t	A–x	K
3.3	.0288	4.46
5.3	.0240	4.08
7.7	.02125	3.52
11.	.01695	3.56
16.8	.0135	3.22
19.5	.0122	3.18
23.3	.0107	3.16
33.1	.00855	2.90
43.8	.00735	2.66

XXIX

3 cc NaOH

t	A–x	K
6.2	.04562	.31
27.2	.03856	.218
51.6	.03183	.222
77.6	.02672	.224
104.8	.02247	.234
123.9	.01938	.254
147.9	.01766	.248

XXX.

6 cc NaOH

t	A–x	K
11.5	.03036	1.136
25.	.02556	.79
32.5	.02277	.74
39.7	.02032	.74
49.5	.01852	.708
61.7	.01533	.728
75.5	.01442	.658
88.6	.01376	.598
104.5	.01321	.548

XXXI.

9 cc NaOH

t	A–x	K
7.4	.02664	2.36
13.4	.01994	2.24
19.4	.01738	1.88
24.4	.01447	2.00
32.4	.01359	1.66
38.5	.01126	1.78
48.5	.01121	1.46
55.4	.01043	1.40
62.4	.01012	1.26

In considering the results the tendency of K to decrease in value is apparent in nearly every case. There are several causes which may unite in producing this result. As free hydroxylamine is slowly decomposed in aqueous solution its active mass in the reaction mixture would be diminished from this cause as time passes. The same effect is produced upon the concentration of the acetone by loss of some of its vapour every time the flask is opened to withdraw a portion. The rapidity of the reaction makes the error due to initial disturbances very large. Furthermore, the values of K are calculated for a bimolecular irreversible reaction, which assumption is probably not quite correct. For, in every case measured, a small but determinable amount of hydroxylamine appeared to be present when equilibrium was attained, a fact which indicates that the reaction is slightly reversible even under these conditions.

For these reasons the constants are not as satisfactory as could be desired. Nevertheless one important point is indicated quite clearly.

The increase in velocity is *not* directly proportional to the amount of alkali added, but is much greater than such proportionality would require. Inspection of the values of K in Tables XXIV, XXV, XXVI and XXVIII shows that as the concentration of the alkali is doubled in each case the velocity is increased approximately *three* times. The difference is striking and persists throughout the course of the reaction as the constant for each series gradually falls off. I cannot believe that it is due to any experimental error. In XXIX, XXX and XXXI, carried out by the iodine method, the same relationship exists. The values of the constants obtained in this series are lower than those given by similar concentrations of the catalyzer when the reaction is followed by acidimetry, a fact probably due to the changes occurring during titration by the latter method. But the same relative rise with increase in the amount of catalyzer is observed in both series.

The increase in velocity of oxime formation is therefore not directly proportional to the concentration of the alkali for the range of concentration here investigated. My former statement[1] to the contrary must then be corrected and the mechanism of the reaction studied with this fact in mind.

[1] Amer. Chem. J., 39, 305.

PART II. ON THE USE OF THE HYDROGEN ELECTRODE IN THE PRESENCE OF ORGANIC SUBSTANCES.

When an oxime is formed by the reaction between a carbonyl compound and a salt of hydroxylamine, the total amount of oxime formed is of course equal to the amount of hydroxylamine which disappears. This quantity may be determined in any particular reaction by the analytical method discussed in Part I. But the oxime may exist in solution in three forms: free oxime, oxime salt and oxime cathion, and the quantity measured by the method referred to is equal to the sum of these three. When it became highly probable that the oxime cathion is the real substance which exists in equilibrium with the ketone (aldehyde, etc.), a means of determining its concentration was sought.

As direct measurement of the concentration of this oxime cathion is out of the question, the only feasible method of attack seems to be a differential one involving the determination of the amount of free hydrogen ions which disappear in its formation. That is, the free hydrogen ion concentration at any time will be equal to the known amount of acid added as catalyzer, plus that generated by the reaction

$$R_2CO + NH_2OH.HCl \rightleftarrows R_2C{:}NOH + HCl + H_2O$$

and less any disappearing in the reaction.

$$R_2C : NOH + HCl \rightleftarrows R_2C{:}NOH.HCl$$

Consideration of the various known methods for estimating hydrogen ion concentration showed that only two seemed likely to give satisfaction under the conditions existing in this case, namely, cane sugar inversion and the potential of the hydrogen electrode. Experiments with the former have been described in Part I.

The use of the hydrogen electrode seemed most promising. From the work of Salm[1], Friedenthal[2], Salessky[3], Schmidt and Finger[4], Robertson[5], and many others, it was apparent that the method may be applied with considerable accuracy to even very dilute solutions of mineral acids. Particularly suggestive, however, was the work of Denham[6], who measured the hydrolysis of several inorganic salts and of aniline hydrochloride by this method. The latter instance led to the belief that small amounts of organic substances would not materially affect the measurements.

Realizing the great importance which such a method, if perfected, would have not only as regards the problem in hand but also for the

1 Z. Elek. Chem. 10, 341., Z. physik. Chem., 57, 471.
2 Z. Elek. Chem., 10, 113.
3 Ibid 10, 204.
4 J. Physic. Chem., 12, 406.
5 Ibid., 11, 437.
6 J. Chem. Soc., 93, 41.

study of many other organic reactions, the matter was gone into quite thoroughly. While it may as well be stated at once that no positive results have been obtained, some of the observations made may be of general interest. And for the benefit of future workers along the same line it sems advisable to give here a full account of the methods employed and the difficulties encountered.

Arrangement of Apparatus.

The measurements of E. M. F. were made by the ordinary Poggendorff zero method, a Rowland-d'Arsonval wall galvonmeter of sensibility serving as the current indicator. As the source of current two of the largest size Leland-Edison cells, in series, were used at first. For a few weeks they showed a comparatively small and regular drop in potential when connected through a resistance of two hundred and fifty ohms. This was tolerable, though inconvenient. Very soon, however, they became subject to sudden and large fluctuations, which tendency was not corrected by placing them in the constant temperature bath. The cause of the trouble was never discovered, but it become necessary to discard them in favor of an ordinary storage cell. When well charged and then connected over two hundred and fifty ohms resistance for twenty-four hours a potential is shown at the end of that time, which remains steady enough for convenient use for ten days or two weeks. The standard of comparison was a Standard Weston Cell[1] , its potential of 1.01887 volts at 25° C being the reference value for all measurements recorded. This was protected by the one thousand ohms resistance in the galvanometer with which it was always in series, and further by a very large external resistance which could be cut out when the zero point was nearly reached.

Instead of the very expensive potentiometer, a form of bridge was devised which served admirably. It consisted of an ordinary metre stick, suitably mounted, and against each end of which three cubes of brass were so fastened that their tops were flush with the surface of the metre stick. In these were soldered five strands of No. 38 manganin wire[2] (0.1 m. m. in diam.) of about fifty ohms resistance per metre, which were stretched along the bridge in such manner as to afford about two hundred and fifty ohms resistance between the poles of the storage cell connected to binding posts, *A* and *B*. One pole of the Weston cell (or of the hydrogen electrode) was also connected to *A* and the other, after going through the galvanometer and a resistance box, to binding post *C*, which was in turn connected below the board with the brass strip, *D*, running along the edge of the metre stick. The sliding contact consisted of a hard rubber block so cut out that the lower pro-

[1]For the loan of which I am indebted to the Bureau of Standards at Washington.

[2]The unexpected durability of this wire should be mentioned. Some difficulty was experienced in mounting it, but once on, the apparatus has been used for six months without breaking a strand.

jections rested upon and moved along the board upon which the metre stick was mounted. It was made to fit the stick so closely that the brass strip *D* was always in contact with a similar copper band inside the block. To this strip of copper five bands of spring copper were connected. By inserting the hard rubber plug in the hole above any one of these strips its end could be pressed down upon the wire below it and thus connection could be obtained between *D* (and therefore C) and any point upon any wire.

When insulated from the table by means of porcelain cleats there was no appreciable leakage except in very damp weather. It was necessary, however, for the operator also to be insulated from the ground unless care was taken to avoid touching any part of the apparatus except the hard rubber when working the contact. A Leeds and Northrup potentiometer, type K, was used instead of this bridge for one series of measurements, the comparative values obtained being as follows:

TABLE XXXII.

Conc. of HCl	v (bridge)	v(potentiometer)
0.10038 N	0.4018	0.4009
.01 N	0.4574	0.4561
.0008 N	0.5175	0.5165

The results are therefore quite satisfactory. Though not as convenient in operation as the direct reading potentiometer, the labour of calculating may be minimized by preparing a table indicating the value of one millimetre division in volts for each successive value of the voltage in the storage current. When, for example, the potential of the storage cell is 2.063 volt, each m. m. on the wire $= \frac{2\ 063}{5000} = 0.4125$ millivolt. Since readings can be made with ease to 0.2 millimetre, it is obvious that the apparatus is capable of more accurate work than the other experimental errors make necessary in any work heretofore done with the hydrogen electrode.

A bath containing about one hundred litres of water was used to maintain the necessary apparatus at constant temperature. It was electrically heated and regulated by the methods employed in this laboratory and maintained at 25° C $\mp$ 0°.01 during any experiment. The stirring was accomplished by means of a vertically running fan motor mounted upon a heavy tripod which sat in the bath. Within the water bath were smaller oil baths for the insulation of the Weston cell and the hydrogen electrode apparatus.

The hydrogen was prepared by the action of pure hydrochloric acid and zinc, scrap platinum being added to facilitate the action. The gas was generated in a Kipp provided with an extension tube above to secure greater pressures. It was then passed through a strong solution of sodium hydroxide to remove any acid and afterwards through a

tube filled with palladium asbestos maintained at 200° to 300°, which should have caused any oxygen present to combine with hydrogen. From this it was passed into the washing apparatus (Fig 1) especially designed to saturate the gas with the same solution as the electrode contained and to avoid the presence of air. After passing hydrogen through the apparatus till all the air was removed, *B* and *C* were closed and the hydrogen bubbled through the solution contained in the funnel above *A*. When this was saturated, *C* was opened and enough liquid allowed to enter to fill the second bulb half full; then *A* was closed and the arrangement was complete. By having a branch tube, *T*, from the hydrogen supply connected with the three-way stop cock at *C*, the liquid could be forced out at *B*, when necessary, without introducing any air. The electrode apparatus is also shown in Fig. 1, but can be more advantageously described a little later.

The platinum electrodes were prepared in the usual way. Each consisted of a platinum plate about 1.5 by 2.5 cm. welded on to a platinum wire, which was fused into a small glass tube. This was supported by the rubber stopper of the electrode vessel and contained a drop of mercury for making contact with the electrical measuring apparatus. The electrodes were platinized in the usual way with Lummer and Kurlbaum solution, treated with hot dilute hydrochloric acid, washed, electroyzed—as cathodes—in dilute sulphuric acid for an hour, and finally boiled for several hours in distilled water. One gauze electrode was prepared by weaving together with fine platinum wire the edges of two platinum wire "baskets" from a broken Linnemann fractionating column. This gave a gauze spheroid, which was fused on to the end of the hydrogen inlet tube. It could be entirely immersed in the solution without affecting the potential, since there was always gaseous hydrogen in contact with the inside. A fine platinum wire passed up the inside of the glass tube, was fused through it outside the vessel and made contact with a small mercury cup on the outside. This electrode was plated with gold and then with iridium [1] with the usual precautions.

Standard normal and tenth normal calomel cells were prepared and used as the subsidiary electrodes. It was desired to measure, if possible, the hydrogen ion concentration of reaction mixtures where such concentration would vary with the time. Calculation of the contact potential between such a solution and the calomel electrode was therefore impracticable. Recourse was had to the use of a saturated solution of ammonium nitrate between the two electrodes. This procedure is stated by Abegg and Cumming[2] to annul the contact potential, and on this assumption was so used by Denham[3] . That it does not do so entirely is shown by the following data for a cell arranged

[1] On recommendation of Prof. F. G. Cottrell; private communication.
[2] Z. Elek. Chem., 13, 17.
[3] Loc. cit.

H electrode — HCl — xN NH_4NO_3 (satd) — 0 1N KCl — Hg_2Cl_2 — Hg

TABLE XXXIII.

x	v	dv	dv (calc.)
1.0038	.3400		
.10038	.4018	.0618	.0552
.01	.4574	.0556	.0575
.001	.5120	.0554	.0586

The normality of the acid used is given under *x;* under *v* is the voltage read; under *d v* is the difference in voltage for two successive concentrations of acid; *d v, calc* is the theoretical difference in the potentials of two concentrations of acid as calculated from the expression

$$v = 0.0592 \log \frac{c_1}{c_2}$$

(the dissociation of the hydrochloric acid being taken into consideration in computing c_1 and c_2) on the assumption that all contact potential has been eliminated by the ammonium nitrate solution. According to this assumption the values in the third and fourth columns should be identical; the fact is that they are not only different but one series increases as the other diminishes. These facts prohibit the use of this expedient in any absolute measurements, but it is quite possible to apply it (in solutions 0.1 N or more dilute) in the measurement of relative differences in potential which was all that was desired in work of this kind. For by measuring the potential given by a number of concentrations of acid and plotting the voltage recorded against the known hydrogen ion concentrations, it is possible to obtain a curve which will give very accurately the hydrogen ion concentration corresponding to any other voltage read under the same conditions.

The Measurements.

As a check upon the accuracy of the method the potentials given by several solutions of hydrochloric acid of known concentrations were first measured. After some practice, involving a number of preliminary experiments, I was able to obtain definite and accurately reproducible values. A practically constant potential was registered within ten or fifteen minutes, though a slight drift, in the tenths of millivolt, could usually be noticed for one or two hours. As a specimen the following data from an experiment with 0.10038 N hydrochloric acid may be given:

TABLE XXXIV.

Time	Voltage	Time	Voltage
		3:08	(Started)
11:05	(Started)	:12	.4018
:15	.4011	:28	.4020
:31	.4013	:59	.4018
:56	.4015	4:25	.4018
12:30	.4020	:40	.4018
:58	.4017	5:20	.4018

The same solution was used in both instances; the current of hydrogen had been discontinued between the two experiments. The same solution was further allowed to remain in the cell in contact with the electrode for two days, no hydrogen being passed in. At the end of that time the hydrogen was turned on and after running for ninety minutes the potential was 0.4019 volt.

Similarly satisfactory results were obtained with 0.01 N hydrochloric acid. When 0.001 N acid was used the high resistance of the solution diminished the sensitiveness of reading. (This cell was measured with the potentiometer.)

TABLE XXXV.

H electrode — 0.001 N HCl — (satd.) NH_4NO_3 — 0.1 N KCl — Hg_2Cl_2 — Hg

	Voltage.
11:00 A. M. (Started)	
11:12	.5095
:24	.5080
:35	.5075
1:00	.5100
2:10	.5090
	Average, .5088

When solutions contain neutral salts (as would be the case in nearly all reaction mixtures) the conductivity is increased and hence more dilute acids can be read with greater accuracy than here shown.

I next undertook to repeat Denham's [1] experiment upon the hydrolysis of aniline hydrochloride. Aniline, repeatedly distilled fractionally, was dissolved in ether and dry hydrochloric acid gas passed in to saturation. The perfectly white hydrochloride was filtered off, washed with ether and dried in vacuo over sulphuric acid and solid potassium hydroxide. For a sixteenth normal solution 4.0478 gm. of this salt was dissolved and diluted to 500 cc. with conductivity water; 48.03 cc. of this solution gave 0.4302 gm. Ag Cl, corresponding to 99.93

[1] J. Chem. Soc., 93, 41.

per cent. of the theoretical.

It had previously been found that the maximum potential is reached much more quickly if the platinum electrode was saturated with hydrogen before the introduction of the solution to be measured. A rapid determination of the potential was especially desirable when working with these organic substances where decomposition may always be feared. So in all the succeeding experiments hydrogen was led into the electrode vessel for from thirty to ninety minutes before the introduction of the solution.

Having saturated the electrode in this manner, a portion of the N/16 aniline hydrochloride solution was introduced against a rapid current of hydrogen. Potentials were recorded as follows:

TABLE XXXVI.

(t = number of minutes after starting the experiment.)

t	Volt.
6	.4973
10	.4986
35	.4975
55	.4969
74	.4969
137	.4964
184	.4964

Accepting 0.4969 as the correct voltage and 0.6192 as the potential of the 0.1 N calomel cell used, this corresponds to 3.81 per cent. hydrolysis, Denham's value for the same concentration was 1.77 per cent. A hitherto unused portion of the N/16 solution was then diluted to twice its volume; when measured under the same conditions as above a voltage of 0.5040 was recorded. Calculated in the same way this corresponds to 5.79 per cent. of hydrolysis, as against Denham's 2.61 per cent. and Bredig's [1] 2.58 per cent. for the N/32 solution.

A solution of 0.000806 N hydrochloric acid was then prepared; this would have the same hydrogen ion concentration as a N/32 solution of aniline hydrochloride if the latter is 2.58 per cent hydrolysed. The potential recorded was 0.5170 ∓ 0.0005 volt—0.013 volt higher than the maximum value given by the aniline hydrochloride solution.

In both of the experiments with solutions of this salt it was observed that when the measurements were finished the solution in the cell had acquired a very decided pink colour. Portions of the same solution which had been left in the vessels in which they were prepared showed at most only a faint suspicion of colour. To test this point more thoroughly some of the fresh solution was placed in a small vessel and a platinized electrode immersed in the liquid. The

[1] Z. physik. Chem., 13, 289.

vessel was closed to the external air, but no attempt was made to remove any oxygen which was present. After a few hours a decided pink colour was produced and deepened decidedly on allowing the test to stand over night. A like result was produced by the iridium electrode. The colour was not diminished when hydrogen was bubbled through the solution. When either hydrogen or air is passed for thirty minutes through a fresh solution in the *absence* of an electrode, no colour can be observed. With one of the electrodes present the colour is quite marked by the end of that time.

These facts pointed strongly to oxidation effects produced by occluded oxygen in the spongy metal which possesses such marked and well known catalytic activity. Hoping to minimize any such trouble I decided to use dimethyl aniline hydrochloride where the liability to oxidize is less. These solutions were prepared by dissolving a weighed amount of carefully redistilled dimethyl aniline in the corresponding measured volume of standard hydrochloric acid and diluting to the strength desired. Repeated experiments with 0.02 N and 0.01 N solutions prepared in this way showed that in every case the potential rose to a maximum value within 15 to 30 minutes and then began to slowly fall away. If the electrode was not removed, the vessel kept closed and the hydrogen flow uninterrupted, this falling off would usually amount to only 1.5 to 2 millivolts for even as long a period as eighteen hours. But if the platinum electrode was removed for some time, thus being brought into contact with the air, the highest value obtainable after replacing it was always from 40 to 120 millivolts less than that recorded in the first instance.

So far only a single platinum black electrode (designated Pt_1) had been used with the dimethyl aniline hydrochloride solution. The effect of a second of the same kind (Pt_2) and of the iridium one (Ir_1) was now investigated. It soon became apparent that each of these three metal electrodes gave a different value. In a solution of 0.02 dimethyl aniline hydrochloride Ir_1 gave a maximum potential of 0.5316 volt in 27 minutes. It was removed and replaced by Pt_2 in the same solution; in 26 minutes this gave a maximum of 0.5036 volt, falling off to 0.5028 after 22 minutes more. Ir_1 was then replaced; 0.5276 volt was recorded in 7 minutes, falling off to 0.5256 after remaining 46 minutes longer. Pt_1 was now introduced and gave 0.5120 volt in 13 minutes. Ir_1 was introduced for the third time and gave 0.5158 volt in 17 minutes, only decreasing to 0.5148 after 77 minutes more. Pt_2 gave 0.4882 and finally Pt_1 registered 0.4958. These results may be exhibited in the following table: the first column gives the order in which the electrodes were introduced, under "time" is given the number of minutes between introduction of the electrode and the reading of the maximum potential in each case.

TABLE XXXVII.

	Ir_1		Pt_2		Pt_1	
	Time	v	Time	v	Time	v
1	27	0.5316				
2			26	0.5036		
3	5	0.5276				
4					13	0.5120
5	17	0.5158				
6			4	0.4882		
7					9	0.4958

Between the removal of Ir_1 at the close of (1) and its introduction in (3), fifty-two minutes had elapsed, during which time it had been kept in a closed vessel containing some of the same 0.02 N dimethyl aniline hydrochloride solution saturated with hydrogen. It was therefore only in contact with the air while being transferred from one vessel to the other; the loss in potential here was 40 millivolts, 0.5316 to 0.5276. Between (3) and (5) it was exposed to the air continuously for 97 minutes; the loss here was 120 millivolts.

The metal electrodes were naturally suspected of occasioning these peculiar results. But when a check experiment was carried out with 0.01 hydrochloric acid the next day all these quickly reached the same maximum value (differing not more than 0.5 millivolt among themselves). On removing an electrode and leaving it in contact with the air for an hour the same original value was restored within 8 minutes after replacing it and remained constant indefinitely.

These results strengthened the opinion that the disturbing influences must be due to oxidation phenomena at the surface of the platinum black. As a final effort to do away with such a possibility the following experiment was carried out: The electrode vessel was filled with hydrochloric acid, the platinum electrode inserted and the vessel tightly closed by means of the well-fitting rubber stopper. Purified hydrogen was then passed through the apparatus for an hour, especial care being taken that only mercury joints or ground glass ones sealed with marine glue should be used in the hydrogen purifying train. The platinum electrode was now made cathode to a three-volt circuit, the anode being a heavy platinum wire inserted in the funnel *F* (Fig. 1). This electrolysis was continued over night, a slow stream of hydrogen being in the meanwhile passed through from the generator in order to produce a slight outward gas pressure in the outlet tube *G*. The next morning the anode was removed from *F* and *G* was closed. By closing *K* and opening *H* and *L* the acid was forced out of the apparatus at *M* by a rapid stream of hydrogen. *E* having been washed out and filled with a fresh N/16 solution of aniline hydrochloride, *L* was closed and *K* opened. The pressure of the hydrogen maintained the solution in *F*

and the gas was allowed to bubble through it for half an hour to remove air. *G* was then opened and the solution, now saturated with hydrogen was allowed to flow into and fill the vessel *E*. It was then forced out at *M* as the acid had been before. The electrode and container were washed out in this way three times by liquid through which hydrogen had been passed for at least thirty minutes in each case. Finally a fourth portion of the solution was similarly saturated with hydrogen in *F*, allowed to flow into *E*, and the apparatus connected up with the calomel electrode as usual by means of the saturated solution of ammonium nitrate. A normal calomel electrode was used in this case, instead of the tenth normal employed in the preceding experiments. The voltage read was as follows, the first column of figures showing number of minutes:

TABLE XXXVIII.

t	Volt.
5	.4555
11	.4563
25	.4563
46	.4561
130	.4554

This potential was so close to that recorded by Denham for the same solution (0.4567) that I hoped the difficulty had been overcome, but further investigation proved the coincidence to be only accidental. When a second experiment was carried out with the same precautions, but using another platinum electrode (which was electrolysed, just as in this case), only 0.4490 volt was shown, even after running for several hours. Similar discrepancies were shown by the two platinum electrodes in N/32 solution of the salt, every precaution being taken as described above. One gave 0.4662 volt and the other 0.4611 as the maximum. Yet these two behaved normally with 0.01 N hydrochloric acid. No further work was done in this fruitless field.

Before such results had been obtained with the aniline compounds certain preliminary experiments were carried out with hydroxylamine hydrochloride solutions preparatory to the oxime work. After some preliminary experiments fairly constant potentials were obtained with a N/32 solution of this salt which indicated hydrolysis amounting to 6.5 to 11.8 per cent., as against 0.74 per cent. found by Winkleblech [1] at the same dilution. The solutions were then analysed for hydroxylamine by the iodine method. Ten cc. of the original solution required for oxidation 10.40 cc. of a certain solution of iodine; 10 cc. of the same solution which had been used in an experiment and was in contact with the platinum electrode for 85 minutes required only 7.67 cc.

[1] Z. physik. Chem., 36, 546.

of the same iodine. Some of the same stock solution was used in another experiment in which it remained in contact with the electrode for 260 minutes; 10 cc. of it then required only 4.31 cc. of iodine—a decomposition of 58.6 per cent. Bright platinum electrodes produced little or no decompostiion, but gave low and unsteady potentials. Knowing[1] that tin has little decomposing action on even free hydroxlyamine I attempted to use block tin plates on which spongy tin was deposited. The potential given by such an electrode was practically independent of the concentration of the acid surrounding it.

Returning to the plated platinum electrodes, I found that by separately saturating the electrode and the solution with hydrogen a very constant value could be obtained within 5 to 10 minutes after bringing them together. In this time there could be little decomposition of the hydroxylamine and this was still further retarded when free acid was present. In this way a solution of 0.025 N hydroxylamine hydrochloride in 0.0125 N hydrochloric acid gave a potential 0.5 to 0.7 millivolt lower than that given by the pure acid of the same concentration. Similarly a solution 0.025 N with respect to acetone and 0.0125 N with respect to hydrochloric acid gave only 0.3 millivolt lower than the pure acid. But when both hydroxylamine hydrochloride and acetone were present the results were quite different. In several cases the maximum potential thus obtained indicated a hydrogen ion concentration about double that which was possible if the hydroxylamine and acetoxime hydrochlorides were completely hydrolysed.

Conclusions.

In the above I have summarized the results of a large number of experiments under varying conditions and extending over several months. After every source of error of which I can conceive has been eliminated as thoroughly as possible, the results are still unsatisfactory. Platinum electrodes which give normal and concordant potentials in solutions of mineral acids are unreliable when certain organic compounds are present. The values then recorded vary with the time, the individual electrode and the exposure of the same to the air; the electrical measurements are accompanied by chemical change, as shown by the colour produced in aniline hydrochloride solutions and the measured decomposition of hydroxylamine. That these chemical changes are intimately connected with the peculiar potential effects observed appears to be certain, but the exact relation between the two is unknown and speculation upon that point seems useless at present. It may be definitely stated, however, that until some means of obviating these chemical actions or of evaluating them is worked out, the potential of the hydrogen electrode cannot be regarded as a safe measure of hydrogen ion concentration in solutions containing certain organic compounds.

[1]Mackay.—P. Nova Scotia Inst. Sci., XI (2), 324.

BIOGRAPHICAL.

Lucius Junius Desha was born near Cynthiana, Kentucky, June 14, 1883. He received his secondary education at the Lockhart School and Public School of that city. From 1900 to 1903 he was employed as bookkeeper in the Farmers National Bank and the National Bank of Cynthiana.

In September, 1903, he was matriculated in Washington and Lee University and was graduated from that institution with the degree of Bachelor of Arts in 1906. He remained in residence there as a graduate student in Chemistry during the session of 1906-7. During the sessions 1907-09 he has been a graduate student in Chemistry in the Johns Hopkins University, with Physical Chemistry and Mathematics as subordinate subjects.

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